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Thesen der Dissertation

Investigation of the applicability of wetland biomass for producing hydrochar by hydrothermal carbonization and its effectiveness for the adsorption of ammonia

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- *The hydrothermal carbonization process can be used to develop the characteristic of biomass and produce a sterile solid product*

  Some properties of biomass make it unsuitable for use as energy feedstock, in carbon sequestration or improvement of soil fertility. However, not only does biomass have an interesting internal structure, it also has the advantage of being available in large quantities at low cost. Moreover, non-fossil carbon sources such as biomass present promising renewable energy carrier. Therefore, pre-treatment technologies can be used to develop the characteristic of biomass and convert it into useful and homogenous products, more efficient energy carriers or carbon storage deposits. Hydrothermal carbonization process (HTC) is a thermo-chemical process for the conversion of organic material, which can improve the properties of biomass. Wet biomass can be transformed into carbonaceous materials with no request to be dried before or during HTC-process. When HTC-char is used in heating, large amounts of greenhouse gases emissions can be mitigated compared with the fossil-derived sources of energy. Due to its reaction temperature, HTC-process is seen as an innovative method to convert problematic biomass like bio-waste, sewage sludge and fermentation residue in a renewable, sterile and hygienic solid product.

- *Wetland biomasses can be converted into sustainable carbonaceous materials*

  Due to the increasing demand, the supply of biomass for different utilizations is becoming limited. This is reflected in rising prices of biomass as well as in an area competition between food, feed and energy production. From a global perspective, Germany is one of the regions rich in wetland areas. However, the production of biomass from re-wetted or wetland is not in competition with other agricultural products. They are abundant at low costs and their properties can be improved using treatment technologies, which may give them a higher value. Rapidly growing grassy plants, such as, reed, typha, juncus and carex, belong to the promising sources of plant biomasses. Their short rotation period and abundant content give favorable application possibilities. HTC can be used for the treatment of such biomasses to generate sustainable carbonaceous materials with higher carbon content than the original biomasses.

- *HTC-process parameters have an influence on the HTC-char*

  Depending on the process parameters, HTC-chars produced were carbon rich and chemically similar to lignite or bituminous coal. The color of biomass changed through HTC-process because of the losses of the moisture and light volatile gases at different stages of HTC depended on the process parameters. The changes in color can be as an indicator of the degree of conversion. The characteristics of HTC-char varied with both raw materials used and hydrothermal carbonization parameters as well as the follow-up treatment of HTC-chars produced. The properties of HTC-chars produced from different raw materials at the same process parameter differed from each other. Reaction temperatures and reaction times affected significantly the composition of HTC-chars produced. Higher reaction temperatures and longer reaction times resulted in lower yields of HTC-chars, a significantly decrease in each of oxygen proportion, bulk density and H/C and O/C

atomic ratios. A significantly increase in the carbon proportion and specific surface area were obtained. The variation of catalyst, solid load and particle size had lower effect on the properties of HTC-chars produced than those were by the variation of both reaction temperatures and reaction times. The nature of the raw materials and HTC-conditions as well as the oxidation of HTC-chars with nitric acid influenced the surface functional groups presented on HTC-chars.

- *HTC-chars from wetland biomasses can be used as alternative and competitive adsorbents for the removal of ammonia in aqueous solution*

  Air and water pollutants affect human and animal health and their well-being; they contribute also to environmental pollution. Ammonia (NH3) and ammonium (NH4+) are familiar by-products of animal and agriculture waste as well as the industrial activities. They are undesirable contaminants because of their negatively impact on air and water quality. Some traditional techniques are available for water treatment applications, particularly for the removal of ammonia and ammonium ions. However, associated operational and technical maintenance problems, strict monitoring and control of operating conditions and the high costs of these methods restrict their applicability. Adsorption processes using dry adsorbents is estimated as superior to other methods. Nevertheless, the difficulty of the use of commercially synthetic sorbents such as activated carbon and its regeneration problem requested to investigate and develop alternative effective and cheaper adsorbents synthesized of cheap natural or raw agricultural materials. Such materials can be as potential replacements for the expensive commercial adsorbents and can improve the efficiency of ammonia removal. In recent times, using low cost natural materials, agricultural residue and waste products to produce potential replacements of the expensive commercial adsorbents for the removal of pollutants is a promising approach.

- *The ammonia removal efficiency of HTC-chars is affected by the adsorption parameters in the batch study*

  Batch study using ammonia solution as a model compound were used to measure the adsorption performance of ammonia in aqueous solution onto HTC-chars produced. Adsorbents produced at different reaction temperatures during HTC showed different adsorption performances. The highest ones were with those produced at HTC-reaction temperature of 230 ˚C, especially those produced from reed. The type of raw material, the catalyst used during HTC or the oxidation of the HTC-chars after production affected significantly the adsorption performances. A quite good removal was achieved with a contact time of one hour. Increasing the initial ammonia concentration decreased significantly the removal efficiency rates because of the limited number of adsorption sites on the adsorbent. The best adsorption performance was achieved at pH of solution with 9.35. The removal efficiency rate of ammonia increased with the increase of adsorbent dosage but the adsorption capacity decreased. The catalyst used during HTC-process or the oxidation of the HTC-chars after production affected their chemical structure and might create adsorption sites, which enhanced significantly their adsorption performance. The oxidized HTC-chars became more acidic and ammonia was strongly adsorbed on their surface. As a result, the adsorption performance of

the adsorbents used in batch study were significantly affected by the variation of adsorption parameters.

- *The ammonia removal efficiency of HTC-chars is affected by the adsorption parameters in fixed-bed column study*

  Dynamic fixed-bed column experiments determine the change in removal efficiency with the time. They are requested to attain basic data for direct applications in industrial systems. The fixed-bed column study was carried out using HTC-chars that had the best ammonia removal efficiency in the already performed batch study. In general, lower flow rates during the adsorption process resulted in a longer breakthrough times and times required for bed exhaustion, which increased the lifetime of the adsorbents. The variation of flow rates had a significant effect on the adsorption performances of all adsorbents used. Furthermore, increasing initial ammonia concentrations resulted in lower breakthrough times for all adsorbents used, but the breakthrough capacities were increased. It was seen that varying the bed heights exhibited a change on breakthrough curves. The column saturation times were longer by increasing the bed heights, which enabled a longer lifetime of the column. However, the variation of initial ammonia concentrations and the bed heights had no significant effect on adsorbents oxidizing with nitric acid. Adsorbents prepared from HTC-chars produced from reed, especially after oxidation showed the highest adsorption performances.

- *HTC-chars are regenerable adsorbents. They can be reused several times without loss of their adsorption performances after regeneration*

  In addition to its high adsorption capacity, a good adsorbent must also present a good ability of reuse during multiple adsorption-regeneration cycles, which is substantial importance in the economic development. Regeneration and reuse of the adsorbent material is a crucial aspect to make it more environments friendly and economical. The investigations of the possibility of the regeneration of the exhausted adsorbents were performed for some adsorbents used in both the batch study and the fixed-bed column study. All regeneration tests were carried out at room temperature. The exhausted HTC-chars were regenerable and could be reused even many times. The best regeneration results were achieved using HCl solution as a regenerant. The highest regeneration efficiency was found with the oxidized HTC-chars, especially with those produced from reed. A decrease in the adsorption performance after regeneration was found with some adsorbents used.

- *HTC-char from wetland biomasses can be used as a filter material as an alternative for activated carbon*

  HTC-char is a low-cost adsorbent with many potential environmental applications. The exhausted HTC-char can be applied directly as fertilizer with no need to be regenerated. The results of this work confirmed that it was possible to transform these wetland biomasses into higher value carbonaceous products with a sufficiently high efficiency for ammonia removal in aqueous solution, which could be designed as a filter. The advantage of using HTC-char of reed as adsorbent for

ammonia removal exists not only because of its highest adsorption performance, but also of its highest char yield and its higher affinity for regeneration. In this respect, recent HTC-chars produced from wetland biomasses, especially those from reed are giving promising results in terms of regenerative ability, because it can be reused several times without a significant decreasing in its removal capacity after regeneration process. The regeneration of adsorbents extends their lifetimes and makes them ecologically and economically feasible. The potential regeneration and reuse of adsorbents used can minimize the need of raw material, which make them more sustainable for the environment and result in a less energy consumption for producing new adsorbents.

- *Perspectives and further research needs*

  One of the most crucial challenges in the biochar industry is the inability of measuring and characterizing the quality during the carbonization process continuously, which is a key property and will open an enormous potential for carbonization engineering.

  Furthermore, controlling how to produce a particular quality of HTC-char for a specific application is of importance in the process engineering design, especially because the researches aim to develop new technologies. The achievement of this objective will be through a planned future project realized. The predicated method for this purpose (DE 102016125286A1) is patent-pending process. The main goal of our future works is a product with a wide range of uses, storage stability and transportable.